UCRL-MA-133867

ES&H manual

Environment, Safety, and Health

Volume II

Part 14: Chemical

Document 14.3
Toxic, Corrosive, or Reactive Gases

Recommended for approval by the ES&H Working Group

Approved by: Robert W. Kuckuck
Deputy Director for Operations

New document or new requirements

Approval date: August 21, 2000

Minor revision, no new requirements

Approved by: The Hazards Control Department

Approval date: June 28, 2004

Revision 2

This work performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

14.3

Toxic, Corrosive, or Reactive Gases*

Contents

* **Minor revision**

Tables

Figure

14.3

Toxic, Corrosive, or Reactive Gases

1.0 Introduction

Compressed gases are traditional tools of research and industry. This document provides requirements and guidance for designing, controlling, and handling toxic, corrosive, or reactive gases as well as procedures for responding to emergencies.

Appendix A contains the terms and definitions used in this document. Compressed Gas Cylinder Sizes and Internal Volumes lists the sizes and volumes of compressed gas cylinders by manufacturer. In addition, please see the LLNL List of Toxic, Corrosive, or Reactive Gases. The LLNL List of Toxic, Corrosive, or Reactive Gases lists compressed gases and their health and reactivity hazard ratings, which are taken from National Fire Protection Association (NFPA) Standard 704. When conflict exists among the respective ratings of the NFPA, the Hazardous Materials Information System (HMIS), or those established by the Occupational Safety and Health Administration (OSHA), then the highest rating applies. Contact your ES&H Team industrial hygienist for ratings that are not included in this table.

The scope of this document is the safe handling of toxic, corrosive, or reactive gases with NFPA/HMIS hazard ratings ≥2. The guidance and requirements in this document only apply to toxic, corrosive, or reactive gases and materials that are handled like gases (e.g., organometallic compounds, such as trimethyl gallium).

Silane and disilane are covered by this document, even though they have Health and Reactivity ratings <2 because the control technology for silane is the same as for other gases covered by this document.

2.0 Exemptions

The full provisions in this document do not apply to:

- Small quantities as shown in Table 1. Only the reduced requirements of Section 3.4 and administrative requirements of Sections 3.1 and 3.2 will apply in some cases, as specified in Table 1.
- Brief, experimental uses as described in the bullets of the third paragraph of this section.
- Several miscellaneous items described in the bullets of the fourth paragraph of this section.

Table 1. Controls for toxic, corrosive, or reactive gases based on the National Fire Protection Association/Hazardous Materials Information System(NFPA/HMIS) health and reactivity* ratings.

Health or reactivity rating is	AND the quantity of gas is	THEN apply the controls in section[a]
0 or 1 (for both)	Any	3.6
2, 3 or 4	Sufficiently small so expanded gas will be diluted below the Occupational Exposure Limit if the cylinder contents leak into room volume or 10,000 ft^3, whichever is less	3.1, 3.2, 3.6, 3.7[b]
2	Any non-exempt quantity	3.1[c], 3.2, 3.6, 3.7
3 d	A single cylinder capacity of 10 liters or less, or ≤5 lecture bottles of ≤0.44 L each. or More than the capacity of 10 liters contained in one or more cylinders.	3.1–3.2, 3.4[e], 3.6, 3.7 3.1–3.3, 3.6, 3.7
4	Equivalent to ≤5 lecture bottles of ≤0.44 L each. or A capacity of more than 5 lecture bottles of ≤0.44 L each, up to 10 liters, in a cylinder or cylinders or Equivalent to more than a capacity of 10 liters.	3.1–3.2, 3.4[f], 3.6, 3.7 3.1–3.3, 3.6, 3.7 3.1–3.3, 3.5 - 3.6, 3.7

* **For compressed gases, assume the contents of a lecture bottle expand to fill 56 L and the contents of a 10 L capacity cylinder will expand to fill 1510 L at normal temperature and pressure (NTP). The expanded volume of liquefied gases needs to be computed on a case by case basis based on the mass of liquefied gas contained in the cylinder and assuming a mole of gas fills 24.45 L at NTP.**

a **See Document 18.1, "Pressure," in the *ES&H Manual* for the necessary controls.**

b **Controls will be required if the gas creates an additional hazard (e.g., simple asphyxiation or flammable mixture) not related to toxicity.**

c **Controls of Sections 3.1.1, 3.1.2, and 3.1.4 apply.**

d **Specific requirements of Sections 3.3.3 and 3.3.9 through 3.3.10 may be waived for portions of gas systems located outdoors, but only with the written consent of the ES&H Team industrial hygienist.**

e **Quarterly inspections of the cylinder and gas delivery hardware, inspection log, an annually reviewed Safety Procedure (SP) or Hazard Assessment, and Control form (HAC) and an Environmental Safety Note (ESN) are required if the gas is used for 90 days or more. The RI and ES&H Team determine if a HAC is sufficient or if an SP is also needed.**

f **Quarterly inspections of the cylinder and gas delivery hardware and an annually reviewed SP and ESN are required if the gas is used for 30 days or more.**

Small quantities due to small cylinder size or dilute mixture (<10 x occupational exposure limit) in the cylinder are exempt. A toxic gas or gas mixture is exempt from the requirements in this document when the quantity is so small that if the entire

contents of a cylinder were to bleed into the room or into a volume of 10,000 ft^3, whichever is smaller, the concentration would be less than the Occupational Exposure Limit (OEL). The ES&H Team industrial hygienist makes this determination, and shall recommend controls for the conditions of use, toxicity, flammability, odor, irritant, and reactivity properties of the gas.

Brief, experimental uses of toxic, corrosive, or reactive gases are exempt from the requirements of Section 4, but not from the controls specified in Section 3.4, in either of the following cases:

- The cylinder contains no more than the molar equivalent of one lecture bottle (0.44-L internal capacity) of gas with a health or reactivity hazard rating of 4, and will be in use (or connected and ready for use) for no more than 30 days.
- The cylinder has a capacity of 10 liters or less, contains a gas with a health or reactivity rating of 3 or less, and will be in use (or connected and ready for use) for no more than 90 days.

The following miscellaneous items are exempt from the requirements of this document:

- Gases with health or reactivity ratings of 0 or 1 (e.g., SF_6).
- Gases that are only flammable (e.g., H_2, methane).
- Inert gases (e.g., He, N_2, Ne, Ar, Xe, Kr).
- Oxygen.
- Fluorine. Guidance on the use of fluorine can be found in Document 14.6, "Safe Handling of Fluorine," in the *Environment, Safety, and Health (ES&H) Manual.*
- Equipment containing a small amount of gas (e.g., an excimer laser or gas spectrograph) that is occasionally recharged from a gas cylinder.

Contact your ES&H Team for the safety controls for such equipment and materials.

3.0 Controls for Working with Toxic, Corrosive, or Reactive Gases

This document specifies controls for toxic, corrosive, or reactive gases, except for fluorine and halogen fluorides, with a health or reactivity rating ≥ 2, and imposes further controls for gases with a health or reactivity rating ≥ 3 based on both the rating and quantity of gas involved. See Document 14.6 for requirements related to fluorine and halogen fluorides. Contact your ES&H Team for the ratings of gases. The controls in Sections 3.1, 3.2, and 3.6 apply to all gases covered in this document; those in

Section 3.3 apply only to gases with health or reactivity ratings of 3 and 4. Section 3.4 contains a reduced set of requirements for brief, experimental uses of toxic, corrosive, or reactive gases with a health or reactivity rating of 3 or 4. Section 3.5 gives additional requirements for the use of high-hazard gases (health or reactivity rating of 4). Section 3.6 describes actions to be taken during emergencies involving these systems. Section 3.7 specifies how to transport poorly labeled cylinders or cylinders containing unknown gases. A summary of applicable controls is found in Table 1.

3.1 Administrative Controls

3.1.1 Planning and Documentation

Whenever an operation involves the use of a toxic, corrosive, or reactive gas, Responsible Individuals (RIs) shall prepare an Integration Work Sheet (IWS) to identify potential hazards, controls, and authorize the planned work in accordance with the requirements of Document 2.2, "Managing ES&H for LLNL Work," in the *ES&H Manual*. All toxic, corrosive, or reactive gases involved in an operation shall be listed on this work sheet. The RI shall contact

- The ES&H Team industrial hygienist for completing Section 2 of the Toxic/Corrosive/Reactive Gases Checklist (Figure 1) for
  - The hazard rating of the gas (if not known).
  - Any necessary facility controls, assessments, or controls for using the gas.
  - Procedures for mitigating any hazards associated with the gas.
- The ES&H Team environmental analyst for
  - Requirements for identifying and resolving potential air, water, and hazardous waste issues, including pollution prevention opportunities.
  - Assistance with obtaining permits and National Environmental Policy Act (NEPA) documentation, as required.
- The Facility Point of Contact (FPOC) to
  - Notify him/her of the potential use of toxic, corrosive, or reactive gas(es).
  - Obtain concurrence with IWSs for planned uses of toxic gases in a facility.

The RI is responsible for having the following documents prepared as specified in following sections of this document:

- Safety Plan (SP) as specified in the second following paragraph.
- Hazard Assessment and Control form (HAC) as specified in the third following paragraph.

- Engineering Safety Note (ESN).

Toxic/Reactive Gases Checklist

Section 1: **To be completed by the Responsible Individual (or designee).** NFPA/HMIS Ratings are assigned by ES&H Team Industrial Hygienist

Date: ____/____/____ **Deliver to Bldg./Room/Location:** _____

User's name/employee number: _____

Phone/fax: _____/_____ **E-mail:** _____

Building/Room: _____/_____ **L-code:** _____

Designated alternate/employee number: _____

Phone/fax: _____ **E-mail:** _____

Building/Room: _____ **L-code:** _____

Facility Point of Contact/employee number: _____

Phone/fax: _____ **E-mail:** _____

Building/Room: _____ **L-code:** _____

List the toxic, corrosive or reactive gas being requested*	Quantity	NFPA/HMIS Ratings* Health	React′

Responsible Individual's name: _____ **Date:** _____

Bldg./Room: _____ **E-mail:** _____ **Telephone No.:** _____

Section 2: **To be completed by the ES&H Team industrial hygienist**

Yes	No		
☐	☐	**Is the IWS complete?**	**IWS No.:** _____
☐	☐	**Is a Safety Plan (SP) required?**	**SP No.:** _____
☐	☐	**Is an Engineering Safety Note (ESN) required?**	**ESN No.:** _____
☐	☐	**Is a Hazard Assessment and Control form required?**	
☐	☐	**Is proper storage available?**	

Industrial hygienist's name: _____ **Telephone No.:** _____
(Please Print)

_____ _____ **ES&H Team No.:** _____
Signature **Date**

Section 3. **(To be completed by the Industrial Gases Section)**

Date material ordered: _____ **Date material received:** _____

Purchase order No.: _____ **Release No.:** _____

Date requester notified: _____

* **Corrosive gasses shall be returned two years after the date of receipt.**

Distribution: Industrial Gases Section, Industrial Hygienist, originator, file ES&H Team, FPOC

Figure 1. Toxic/Corrosive/Reactive Gases Checklist, used for acquiring toxic, corrosive, or reactive gases.

An IWS shall be prepared to authorize the planned work in accordance with the requirements of Document 2.2. All toxic, corrosive, or reactive gases involved in an operation shall be listed on this work sheet.

A SP is required unless the IWS indicates that one is not required, as shown on the Toxic/Corrosive/Reactive Gases Checklist (Fig. 1), or if the quantity and conditions of use fall within the limits stated in Section 2.0 about brief, experimental uses of toxic, corrosive, or reactive gases. The FPOC concurs that the planned activity can proceed. See Document 2.2 for direction about when SPs are required.

HACs are used to document the use of personal protective equipment (PPE) and respirators in accordance with the requirements of Document 11.1, "Personal Protective Equipment," in the *ES&H Manual*. A HAC is used for Work Authorization Level (WAL) (Document 2.2) 2 and 3 work when a SP is not required. A HAC is also needed to address PPE and respirator requirements for installing or changing cylinders of gases with an NFPA/HMIS health hazard rating of 2 or more if a SP has not been prepared.

All Safety Plans and HACs shall include the:

- Quantity and type of the toxic gas(es) in storage and use.
- Sizes of the cylinders, tanks, or containers in use and the number of containers manifolded together at any time. (See Compressed Gas Cylinder Sizes and Internal Volumes for further details.)
- Locations where gases are stored and used.
- PPE for routine use and emergencies.
- Procedures for dismantling used equipment.
- Schematic diagram of the gas-delivery system.

ESNs are mandatory for the gases and operations covered by this document, unless the operation is exempt according to Sections 2.0 and 3.4. ESNs shall be prepared in accordance with the guidance in Document 18.2, "Pressure Vessel and System Design," in the *ES&H Manual*, and shall be revised when changes are made in any system handling toxic, corrosive, or reactive gases.

3.1.2 Acquisition by Any Means and Delivery of Toxic, Corrosive, or Reactive Gases

All compressed gas shipments shall go through the Industrial Gases Section. Direct orders and deliveries of gases to requesters are not permitted.

To order toxic, corrosive, or reactive gases listed in the LLNL List of Hazardous Gases (link to it):

- The RI (or his/her designee) shall discuss the planned use of the gas with the ES&H Team industrial hygienist, then complete the appropriate section of the Toxic/Corrosive/Reactive Gases Checklist (Fig. 1).
- The industrial hygienist shall ensure that the planned use of the gas is compatible with LLNL practices for safe use, assign NFPA/HMIS health and reactivity ratings to the gas (or gas mixture), and sign the appropriate section of the Toxic/Corrosive/Reactive Gases Checklist.
- The RI shall submit the Toxic/Corrosive/Reactive Gases Checklist to the Industrial Gases Section before initiating an acquisition. The Industrial Gases Section will not acquire the gas without a completed Toxic/Corrosive/Reactive Gases Checklist.

Once the gas arrives at LLNL, the Industrial Gases Section verifies proper content and DOT labeling, logs the cylinder into the Chemical Tracking System (ChemTrack), and, on the same day of arrival (if the gas is a toxic gas) or within one work day of arrival (if the gas is a reactive gas), delivers the gas to the designated delivery point specified by the requester. If the user or the user's designated alternate is not present to receive the gas, then Industrial Gases will send an e-mail notification to the user, designated alternate, and FPOC advising them which gases were delivered and where.

The requester shall ensure that toxic, corrosive, or reactive gases do not remain in hallways, unoccupied rooms, or uncontrolled areas not normally used for the storage of such gases.

3.1.3 Labels and Signs

Cylinders arrive with labels identifying the proper shipping name (e.g., "Compressed gas, n.o.s."), vendor label, the U.S. Department of Transportation (DOT) Hazard Class, and the United Nations number per regulations established by DOT, 49CFR. The names of gases in mixtures and the concentration and quantity of each gas are needed to guide the safe handling and use of toxic, corrosive, and reactive gases. For example, a cylinder containing 50 ft^3 of 50% carbon monoxide (CO) in a CO:N_2 mixture is more hazardous than a cylinder with 0.5 ft^3 of pure CO and therefore would require more stringent controls.

A label identifying the contents of toxic gas pipes shall be affixed to such pipes every 20 feet, at wall penetrations, and in concealed spaces.

NO SMOKING signs shall be posted in the immediate vicinity where flammable and pyrophoric gases are stored, handled, or used.

3.1.4 Design Specifications

When semiconductor fabrication technology is to be used, specifications for commercial equipment shall comply with applicable provisions of SEMI Standards F-4, F-6, F-13, F-14, S-2 and S-5. Purely administrative provisions of these standards, such as the qualifications of welders, do not apply. Contact your ES&H Team industrial hygienist for details of these standards.

Restrictive flow orifices (RFOs), when available from the vendor, shall be used to control unplanned releases of toxic, corrosive, or reactive gases. If the vendor can not supply RFOs for a specific gas, then consideration shall be given to installing an LLNL-built orifice as close to the cylinder as possible. When included as a passive mitigation measure for a safety class or safety significant system in the facility safety analysis report, RFOs shall be factory installed by the cylinder vendor. Safety analysis at LLNL is discussed in Document 3.1, "Nonnuclear Safety Basis Program," in the *ES&H Manual*.

Cylinders, gas lines, and equipment in which gases are used shall be made of inert or resistant materials. Measures shall be taken to prevent the unplanned mixing of incompatible materials.

3.2 Handling Cylinders of Toxic, Corrosive, or Reactive Gasses

3.2.1 Personal Protective Equipment

The type of PPE needed when handling toxic, corrosive, or reactive gases is determined by the cognizant ES&H Team industrial hygienist and depends on the hazards associated with the gas in use. The PPE for routine or emergency use of toxic, corrosive, or reactive gases shall be specified in the governing Safety Plan or HAC. Respirators are often needed when installing or changing cylinders and when filling vessels or cells with gas mixtures.

3.2.2 Minimizing Quantities

Store and use the minimum quantity of gas needed for the job. However, that quantity should be consistent with the need to minimize the number of hazardous cylinder changes.

3.2.3 Installing and Changing Cylinders

If a cylinder is designed to receive a cap, the cylinder cap and valve cap shall not be removed from the cylinder until you are ready to connect the cylinder to a gas delivery system. The cylinder cap and valve cap shall remain on if the cylinder is to be left unconnected to the system.

When you are ready to install the cylinder:

- Strap the cylinder securely at its use location.
- Remove the cylinder cap and valve cap from the cylinder. Do not use wrenches or "cheaters" to remove the caps because such devices could break the valve and allow gas to escape. Such gas escapes can create a serious hazard to the user and even cause a serious incident.
- Keep the caps removed in step 2 with the cylinder.
- Connect the cylinder to the gas delivery system.
- Before unstrapping a cylinder to be removed, be sure the cylinder valve is closed and the cap has been put back on the cylinder.

3.2.4 Moving Cylinders

- Inspect the cylinder for signs of corrosion or other damage that would make removal dangerous. Call the ES&H Team for guidance if the cylinder cannot be moved safely.
- Install valve plugs as a final barrier against leakage on all cylinders being moved from buildings where they are stored or used. Cylinders shall not be moved without valve plugs. Contact Industrial Gases Section if it is necessary to replace a missing cylinder plug.
- Install the cylinder cap to protect the valve from mechanical damage.
- Ensure that the vendor label on the cylinder identifying its contents is still attached. Ensure that the cylinder retains its DOT labels and that the DOT labels are still legible before the cylinder is moved. Contact Industrial Gases Section if it is necessary to replace worn DOT labels.
- Secure the cylinder, then move it in accordance with the guidance in Document 18.1,"Pressure," in the *ES&H Manual*.

- If the cylinder is to be moved to another location, notify the ChemTrack Operations Group and FPOC of the new location.
- Toxic/corrosive gases shall be moved in accordance with the requirements of Document 21.2, "Onsite Hazardous Material Packaging and Transportation Safety Manual," in the *ES&H Manual* (link here to

  http://www-r.llnl.gov/hmpts/).

  — Gases shall be moved in the bed of a truck, and shall never be moved by bicycle.
  — Requesters shall never move cylinders off-site. Transportation of cylinders off-site shall be coordinated with the Industrial Gases Section.

3.2.5 Storing Inactive Gas Cylinders

The requirements in this section apply to the storage of inactive gas cylinders. Requirements for the storage of active gas cylinders can be found in Sections 3.3.5, 3.3.6, and 3.3.7.

Valve protective devices or caps and gas tight valve outlet caps or plugs shall be kept in place when cylinders are stored, whether they are full, partially full, or empty.

Indoor Storage

- Label each cylinder in accordance with the guidance given in Section 3.1.3.
- Keep incompatible gases 20 ft apart or separated by a 0.5-hr fire barrier. According to NFPA 55, the gas categories used to define compatibility and storage are: toxic, pyrophoric, flammable, oxidizing, and nonflammable. Contact your ES&H Team industrial hygienist for guidance on the compatibility of groups of gases.
- Store cylinders:

  — In areas that are normally locked. Ensure each cylinder is capped and chained (or otherwise secured) to prevent the cylinders from tipping over. (See Document 18.1 for details.)
  — In separate, dedicated storage rooms that are ventilated to remain at negative pressure with respect to other rooms at a rate exceeding 1 cubic foot of exhausted air per minute (cfm) for each square foot of floor area. Exhaust ventilation is not required for gases with an NFPA health rating of 3 or less provided the quantity stored is <650 ft^3 at NTP and, for chlorine, <810 ft^3 at NTP, but should be provided.
    – A manual shutoff labeled "Ventilation System Emergency Shutoff" shall be located next to the access door to the storage area.
    – The exhaust ventilation shall not be recirculated, and

  - The ventilation can be cut off if no hazardous gas is being stored.

- Gases with an NFPA health rating of 4 shall be stored in gas storage cabinets or in exhausted enclosures and arrangements shall be made to ensure that the concentration of gas from the gas storage cabinet or ventilated enclosure does not exceed a predetermined safety level at places where people could be exposed. This may be a treatment system and/or a Restricted Flow Orifice (RFO) and/or other engineering technique. See Document 12.3, "Evaluation and Control of Facility Airborne Effluents," in the *ES&H Manual* for direction on how to fulfill this requirement.
- Only in areas or buildings with automatic sprinkler systems. Water-reactive gases shall be protected from becoming wet during sprinkler discharges.
- In areas with explosion-relief venting when flammable or pyrophoric gases are involved, unless the cylinders are stored in gas-storage cabinets or vented enclosures.

Outdoor Storage

- Label each cylinder in accordance with the guidance given in Section 3.1.3.
- Protect cylinders from sunlight and rain.
- Do not let cylinders stand in puddles.
- Use a canopy (or equivalent) for cylinders that are stored in new outside storage facilities. Older storage sheds can be used for cylinders not containing silane. Make sure the canopy is equipped with an automatic fire sprinkler system if the gas involved is a pyrophoric, flammable, or combustible gas with a health hazard rating of 3 or 4.
- Keep cylinders at least 75 ft away from air-conditioning-system intakes, the site boundary, public ways, assembly points, and buildings not associated with the storage or use of the gases when compressed gases with a health-hazard rating of 3 or 4 are involved.
- Keep vegetation and flammable materials at least 15 ft from the gas storage area.

Exceptions

The following exceptions apply to the storage of inactive gas cylinders:

- An inactive cylinder with its cylinder and valve caps in place may be kept in a gas storage cabinet designed for No. 1 cylinders along with an active cylinder connected to the gas delivery system if both cylinders are smaller

than No. 1 size (see Compressed Gas Cylinder Sizes and Internal Volumes (URL link) for details).

- During brief, experimental uses (see Section 3.4), cylinders containing quantities of gas that are the molar equivalent of up to five lecture bottles of pure gas can be stored and used together.

Silane Storage

Always store silane in a ventilated gas-storage cabinet or, preferably, outdoors under a canopy to prevent accumulation of this unpredictable pyrophoric gas. New silane installations should use outdoor storage under a canopy.

Storage Limit for Cylinders of Corrosive Gas

Cylinders with corrosive gases should not be kept for more than one year and shall not be kept for more than two years.

3.2.6 Guidance for the Return and Disposal of Gas Cylinders

Gas users or designated alternates (e.g., coordinators) are responsible for ensuring that gas cylinders that are empty or no longer needed are disposed of as described below. Half of a cylinder's ChemTrack label shall be sent to the ChemTrack Group when the cylinder is returned or disposed of. For guidance about cylinders of gases not covered by this document, see Document 18.1.

Contents

Before returning or disposing of an empty or unneeded cylinder, verify:

- The cylinder's contents. The cylinder's contents need to be known to ensure safe handling and ultimate disposal; maintaining original labels and other identifying information is essential. Cylinders with unknown contents shall not be accepted by Industrial Gases or Radioactive and Hazardous Waste Management (RHWM) Division, and shall not be returned to the vendor. Identifying unknown materials is time-consuming and costly. Any cylinder whose DOT labels have been damaged or lost or whose contents are unknown shall not be moved or transported. Contact the Fire Department at 911. See section 3.7.
- That the cylinder is empty. A container is defined as "empty" when the pressure in the container is at atmospheric pressure and the valve or burst disc has been removed.

- Whether the cylinder held a hazardous material. A gas cylinder that previously held an acute or extremely hazardous (e.g., reactive, corrosive, or toxic) material and that cannot be returned to the original vendor shall be managed as hazardous waste through RHWM.

Options

Dispose of or return empty or unneeded cylinders in one of the following ways:

- Return to vendor. Every effort shall be made to return gas cylinders to the vendor. All cylinders shall meet DOT regulations for transportation purposes, including knowledge of the contents. Gas cylinders processed through a contract with the Industrial Gases Section may be returned to the vendor. Cylinders returned to the vendor should always have residual gas (i.e., positive pressure) to prevent contamination. Guidance is available from the Industrial Gases Section.
- Send to Donation and Utilization Services (DUS). Contact your ES&H Team and the Industrial Gases Section to have a gas cylinder evaluated for disposal as scrap. Whether defective or not, an empty gas cylinder with valves removed can be sent to DUS for reclamation as scrap. Gas cylinders that previously held an acute or extremely hazardous material, as defined in "Waste Acceptance Criteria" cannot be reclaimed as scrap. (link to

  http://www.llnl.gov/es_and_h/wac_rev2/wac_contents.html
- Handle as hazardous waste. Gas cylinders that contained acute or extremely hazardous material shall be managed as hazardous waste through the RHWM Division. Any cylinder that the generator cannot verify as being empty is not exempt from the hazardous waste regulations, and shall be appropriately managed and handled as hazardous waste.

Cylinder Integrity

Cylinders that do not meet DOT requirements, have been modified, or whose integrity has been otherwise compromised shall be evaluated before on-site transfer. Modified cylinders become either hazardous waste or scrap because they can not be returned to their original function. Contact your area ES&H Team for assistance. Toxic gases shall not be returned to the Industrial Gases Section by users. Contact Industrial Gases to coordinate the pick up and return of cylinders to vendors. Industrial gases will transport the cylinders in accordance with Document 21.2.

3.3 Controls for Facilities and Equipment Using Toxic, Corrosive, or Reactive Gases

See Table 1 for situations where this section applies. All facilities and equipment covered in this section shall have a Safety Plan and an ESN.

3.3.1 Design Criteria

Toxic, corrosive, or reactive gas control relies on minimizing the quantity of gas and enclosing the source, distribution system, and apparatus in which the gas is used. Ventilation is a secondary control measure after minimization and enclosure. Use the following design criteria:

- Storage tanks and cylinders, gas lines, and equipment in which toxic, corrosive, or reactive gases are used shall be designed according to seismic criteria appropriate for the hazard class of the operation. (For further details, see Document 3.1 as well as the requirements in Document 18.1.)
- Ventilation systems shall be designed in accordance with standards of good practice, as specified in the references for Document 12.2, "Ventilation," in the *ES&H Manual*.
- Experimental and process equipment, gas-storage vessels, and delivery systems used for toxic, corrosive, or reactive gases shall comply with the requirements in Document 18.1 and its associated documents.
- Follow the guidance in Document 12.3 to control emissions to the atmosphere.

To reduce the hazard of accidental release and to avoid adverse community relations, the following are recommended as best management practices

- Uniform Fire Code (UFC) Articles 51 and 80 (recommended for all toxic gas systems covered by this document).
- The requirements in UFC Article 51 (recommended for semiconductor facilities).
- The design criteria in UFC Articles 51 and 80 (recommended for experimental and process equipment, gas-storage vessels, and delivery systems used for toxic, corrosive, or reactive gases).

3.3.2 Cylinders

Cylinders, gas lines, and equipment in which gases are used shall be protected from disturbances, such as being struck by falling objects, pedestrians, or vehicles.

3.3.3 Gas Lines

Gas lines shall be:

- Provided with some mechanism to stop the flow of gas at, or close to, the cylinder when hazardous conditions are created by toxic, corrosive, or reactive gases. Appropriate mechanisms can include a valve for an analytical instrument in cases where the cylinder is a few inches or a few feet away from the equipment using the gas, or remote-controlled shutoff valves for semiconductor manufacturing tools that are located tens of feet away and through one or more walls from the cylinder.
- Pressure-tested and leak-tested before use.

Lines that convey toxic, corrosive, or reactive gases shall be constructed of all-welded metal lines or double lines, with the outer line vented. Adhesive-bonded plastic lines with adhesive compatible for the gases being carried (or equivalent gapless construction) may be used if the materials and construction provide safety equivalent to that provided by all-welded or double lines.

Nonwelded connections should be in vented enclosures where the average air velocity through openings is $\geq$200 fpm and the minimum velocity is $\geq$150 fpm. Test smoke released anywhere in the plane of the window or door shall never flow outward.

The purging of gas lines as close as possible to the cylinder is advisable for gases with a health or reactivity rating of 3, but is required for gases with a health or reactivity rating of 4 or for process quality. A manual purging system may be used; an automatic system is optional. The preferred methods, however, are sequential evacuation or chemically inert gas backfilling under automated controls.

3.3.4 Gas Manifolds

Gas manifolds shall be modularly constructed or butt-welded, unless a demonstrably equivalent or superior method is used. The lines for these manifolds shall be made of electropolished stainless steel type 316 or other compatible material. Gas manifolds shall have:

- Excess-flow valves that cut off gas flow in the event of an overflow condition.
- A "connected-poppet" (i.e., tied-seat) regulator for process gases.
- A high-pressure isolation valve and high-pressure vent valve.
- A regulator bonnet relief and regulator overpressure relief valve.
- A sintered-steel filter (or equivalent) with 0.5-µm porosity to prevent fine particulate from fouling components downstream.

- Cylinder connections that comply with the requirements of the Compressed Gas Association (CGA).
- Vent- and purge-line check valves.
- Vacuum Component Rod (VCR)-compatible fittings, unless a demonstrably equivalent or superior method is used.

Gas manifolds shall be pressure-tested to 1.5 times the maximum allowable working pressure (MAWP) by an LLNL Pressure Inspector, or the test shall be certified by the vendor. Written certification is required for helium leak tests. Leak tests also may be conducted using other equivalent or superior method.

3.3.5 Gas Storage Cabinets

Toxic, corrosive, or reactive gases in active use or a ready-to-use condition shall be stored in gas-storage cabinets or vented enclosures (Section 3.3.6) that are constructed of 12-gauge steel or thicker. These devices shall have**:**

- Operational louvers for ventilation at all times, even when the door and window are shut.
- A self-closing and self-latching door.
- A self-closing window (gas-storage cabinets only).
- A manual cylinder shutoff valve or valve-wrench fitting that is easily reachable. The valve handle can be located outside the enclosure or cabinet.
- Listed or approved automatic sprinklers whenever pyrophoric, flammable, or combustible gases are in use. Automatic sprinklers shall be the corrosion-resistant type and installed in accordance with NFPA Standard 13, "Standard for the Installation of Automatic Sprinkler Systems."

The controls for storing toxic, corrosive, or reactive gases in gas cabinets or vented enclosures are as follows:

- Make sure the average air velocity through the cabinet or enclosure window is >200 fpm and the minimum air velocity is >150 fpm at any point. Test smoke released anywhere in the plane of the window or door shall never flow outward.
- Seismically secure the cabinet or enclosure to prevent it from tipping over during an earthquake.
- Do not store more than three cylinders or five lecture bottles in a cabinet.

- Position each cylinder (or component) within the cabinet so that the gauge is easily readable. Rigidly mount the cylinder to the cabinet with the cylinder caps in place; the caps can be removed afterward. A release in which a cylinder vents near the ground is far more serious than a release in which a cylinder vents into a gas-storage cabinet that is connected to a properly designed exhaust system having a tall stack or other controls.
- Make sure that routine operating controls or displays are posted on the outside of a gas-storage cabinet whenever possible. Controls within a cabinet shall be visible and easily readable, and located in a place where the controls can be easily read through the cabinet window.
- Label a cabinet to show the gas(es) being stored.

3.3.6 Vented Enclosures for Gas Equipment

Gas equipment (or a gas apparatus) shall be placed in a vented enclosure when direct venting to a tall stack is not possible, when venting to the atmosphere after treatment is not possible, or when leakage could escape into a potentially occupied space (see Section 3.3.8, "Effluent Discharge and Treatment Systems").

There are many possible design variations for vented enclosures. The general requirements for enclosures used at LLNL are as follows:

- Use vented cubical enclosures with a face velocity of 125 fpm where cross drafts and building air turbulence will not cause turbulence that could sweep air from inside the hood to the outside. Set the equipment back 6 to 12 in. from the face of the enclosure. The ideal cubical enclosure resembles a paint spray booth with a long channel in which incoming air has the longest time to turn back gas escaping from leaks in high-speed jets. Flow-evening baffles or slots can be used in the back end of such enclosures.
- Ensure that
    - Vented enclosures (other than those previously mentioned) have holes for make-up air, or through which the valve handles can pass, and that the air velocity passing inward through the holes is $\geq$500 fpm.
    - Test smoke released near any suction opening does not flow outwards.
    - Ventilation fans are connected to emergency or standby power.
    - Ventilation systems, gas-storage cabinets, vented enclosures, outer lines of double lines, enclosures around connections, purge lines, effluent from experimental or process equipment, and equipment enclosures are vented to prevent hazardous environmental releases and roof-top exposures.

- Use shields or baffles as needed to keep possible sources of gas jets away from the openings of vented enclosures. In the absence of a shield or baffle, a leaking gas jet released near or at an opening will pass through the opening into potentially occupied spaces unless unreasonably high air velocities are maintained at the openings.

3.3.7 Cylinder Overpack/Leaker Cabinet

A "leaker cabinet" (or preferably a cylinder overpack) should be available where more than three gas-storage cabinets or vented enclosures are used to support an operation or experiment. If a leaker cabinet is used, the exhaust should be connected to a stack or effluent treatment equivalent to that for cabinets used to store active gases. Cylinder overpacks and containment kits are commercially available. A leaker cabinet shall be provided if gases with an NFPA health rating of 4 are stored outside of buildings. Alternate means of preventing leaks of gas to the building or atmosphere or leaker cabinets shall be provided for gases with an NFPA health rating of 3 or 4.

3.3.8 Effluent Discharge and Treatment Systems

Effluents shall be discharged after cleaning or filtration through tall stacks or as specified by the ES&H Team Industrial Hygienist. The ES&H Team Environmental Analysts should likewise be consulted to determine if emissions would adversely affect any air or environmental permit limits. For additional information, see Document 31.1, "Air Quality Compliance," in the *ES&H Manual*. Contact your ES&H Team for advice and for the calculations for your system. Calculations are determined in accordance with the guidance given in Document 12.3. Systems shall be designed in accordance with the minimum stack-height requirements to avoid re-entrainment.

Cleaning and filtration methods depend on the chemistry of the gas or byproducts (e.g., plasma-etch effluent) being processed. Equipment that works by pyrolyzing gases to water-soluble products collected in a low-pressure drop scrubber (i.e., a burn box or controlled decomposition/oxidation [CDO] unit is widely used for halogenated gases. Combustion products formed in a burn box or CDO are removed using a low-efficiency water scrubber located downstream from the heat source.

Because a scrubber cannot remove fine particles, burn boxes and CDOs shall not be used to treat some effluents that produce combustion products that are not highly soluble in water, such as arsine. Hydrides can be treated by scrubbing in an oxidizing solution, such as potassium permanganate. Hydrides that form water-soluble byproducts can be treated using a burn box or CDO. Other chemistries can be used as well. For example, arsine can be treated using an easily handled, solid sorbent cartridge.

The following controls apply to all discharge systems:

- Exhaust fans for discharge systems shall be located outdoors.
- All runs of duct work in occupied areas shall be under negative pressure.
- Discharge systems shall have a duct, fan, and enclosure materials that are chemically inert or resistant to the contaminants being handled. However, emergency system duct work designed to endure a limited number of exposures before replacement may be used.
- The ventilation duct work shall be designed to be compatible with the material in use.
- Ventilation of six air changes per hour should be applied to rooms where toxic, corrosive, or reactive gases are stored or used. This ventilation shall be independent of that applied to gas-storage cabinets or ventilated enclosures.

3.3.9 Gas Monitors and Alarms

Work spaces, gas-storage cabinets, vented enclosures, outer lines of double lines, and enclosures around connections shall be continuously monitored for gas leakage by means of electronic detection instruments equipped with or connected to alarms. The exceptions to this requirement are as follows:

- Situations described in Section 2.
- Gases that produce noticeable odor or irritation below their permissible exposure level or toxic concentrations.
- Gases that do not induce olfactory fatigue, provided that all workers receive training and periodic retraining in such warning properties (e.g., odor and irritation).

All indoor storage areas for gases with an NFPA health rating of 4 shall be equipped with gas monitors. Indoor storage areas for gases with an NFPA health rating of 3 shall be equipped with toxic gas detectors unless the odor threshold of the gas is below the occupational exposure limit for NFPA 55.

Other requirements and recommendations include the following:

- Gas monitors located in gas-storage cabinets, occupied areas, and other critical locations should automatically shut off gas flow.
- Alarm set points shall be determined by the area ES&H Team industrial hygienist according to applicable air contamination limits and the equipment in use.
- Both audible and visible alarms should be used. All alarms shall annunciate locally; those used to notify the Fire Department of significant threats to

personnel and property shall annunciate at the Emergency Dispatch Center (EDC). Locations that need EDC annunciation include occupied spaces and areas where flammable gas mixtures could form during credible incidents.

- Periodic maintenance and calibration of sensors and annunciators shall be performed in accordance with manufacturers' recommendations. Calibrations of sensors need to be periodically checked by the manufacturer or an instrument calibration specialty shop under contract. A logbook or record of calibrations shall be kept by the user.
- Vent fans for gas cabinets, outer gas lines, and ventilated enclosures; safety/alarm systems; and gas-monitoring systems shall be connected to an emergency power supply, preferably an uninterruptible power supply.
- Evacuation alarms shall be triggered only by detection of excessive concentrations of gas, and shall not be triggered by malfunctions or power interruptions.
- Alarms shall not be disabled unless the EDC, area ES&H Team, and the FPOC have been notified.

Contact the Hazards Control Department and the Alarms Shop for guidance on sensor types and locations, set points for alarms, and alarm types and locations.

3.3.10 Emergency Eyewashes and Safety Showers

Eyewashes and safety showers shall be provided in areas where exposure to corrosive gases or materials capable of injuring the eyes or skin (e.g., organometallic compounds) could occur. Situations requiring safety showers/eyewashes and administrative requirements for safety showers/eyewashes are specified in Appendix B of Document 14.1, "LLNL Chemical Safety Management Program,"in the *ES&H Manual*. Requirements for training the users of eyewashes/safety showers are found in Section 3.1.3 of Document 10.2, "LLNL Health Hazard Communication Program," in the *ES&H Manual* (for non-laboratory situations) and Section 3.2.6 of Document 14.2, "LLNL Chemical Hygiene Plan for Laboratories," in the *ES&H Manual* (for laboratory situations). Requirements for the testing of safety showers/eyewashes are specified in Appendix B of Document 14.1. Engineering specifications are found in LLNL Facility Standard PEL-M-11610, "Emergency Eyewash & Shower Units."

3.4 Reduced Requirements for Brief, Experimental Uses of Toxic, Corrosive, or Reactive Gases

3.4.1 Documentation

Operations that meet the criteria for "brief, experimental uses" of toxic, corrosive, or reactive gases do not require a Safety Plan or ESN. However, an IWS is required as specified in Document 2.2. Operations that meet the quantity limits but exceed the duration (time) guidelines require a SP or HAC, as determined by the RI as specified in Section 3.1.1 of this document, which shall be reviewed annually. An ESN is required if the operation is to last longer than 180 days.

Equipment used in these operations shall be inspected by the user quarterly, and the results shall be documented.

3.4.2 Storage and Use

Storage and use guidance for cylinders is as follows:

- Cylinders should be stored in a hood or glove box. However, cylinders may be stored outside a hood or glove box if secured and capped as specified in Document 18.1 .
- Cylinders containing quantities of gas that are the molar equivalent of up to five lecture bottles of pure gas may be stored and used together.
- Cylinders with incompatible gases shall not be stored together.

3.4.3 Advance Notice

RIs shall ask the ES&H Team for an estimate of the environmental concentrations of air contaminants that could be created by a system failure. The ES&H Team and the organization using the gas shall make arrangements to ensure that controls are taken to prevent accidental gas emissions and roof-top exposures. This process takes a few days or a few weeks for a gas with known properties and established OEL, and may take longer if exposure limits have to be developed.

3.4.4 Use of Compatible Materials

RIs shall ensure that gases are conveyed using inert or resistant materials (i.e., those that will not degrade or fail during anticipated service).

3.4.5 Limiting or Avoiding Mixing of Incompatible Materials

RIs shall ensure that incompatible materials are not mixed or, when mixing is needed for an experiment, that materials are mixed under controlled conditions that ensure that released energy and reaction products are processed in a manner that protects personnel and the environment. Any mixing of incompatible materials shall be described in the applicable Safety Plan or HAC.

3.5 Use of Significant Quantities of High-Hazard Gas

The requirements in this section apply to the use of significant quantities of high hazard gases (i.e., gases with a health or reactivity hazard rating of 4 when present in quantities >one lecture bottle, and gases with a health or reactivity rating of 3 in a cylinder larger than approximately 7-in. diameter × 19-in. high). An industrial hygienist and pressure safety engineer shall evaluate gas mixtures to determine if these requirements are applicable, or shall specify other controls, as necessary. A safety plan is required.

3.5.1 Leak and Excess-Flow Detection

Leak and excess-flow detection systems with fail-safe defaults in the "closed" position are required where significant quantities of high-hazard gases are in use. These systems automatically shut off gas flow to the cylinder when

- There is an overflow of gas.
- There is a seismic disturbance.
- The gas detection alarm or manual fire alarm in a building or area activates.
- Local operator shutoffs and alarms (or other scenarios) are selected by the RI and the Hazards Control Department.

Leak and excess-flow detection systems shall be positioned in a manner that makes repairs and calibration easy to perform.

3.5.2 Purging, Venting, and Shutoff Requirements

The purging of gas lines as close as possible to the cylinder is advisable for gases with a health or reactivity rating of 3, but is required for gases with a health or reactivity rating of 4 or for process quality. A manual purging system may be used; an automatic system is optional. The preferred methods, however, are sequential evacuation or inert gas backfilling using automated controls.

The following requirements apply when purging, venting, or shutting off gas systems:

- All gas vented from relief valves or openings shall be directed toward the cabinet's exhaust.
- The regulator overpressure relief valve shall be discharged to a vent system.
- The regulator bonnet relief shall be discharged to a vent system or enclosure (see Section 3.3.6–3.3.8).
- The emergency shutoff shall be located outside the gas-storage cabinet and shall be
  - Properly identified.
  - Conspicuous.
  - Easily accessible.
  - Protected from inadvertent operation.
  - Of the red mushroom type.

3.6 Emergencies Involving Toxic, Corrosive, or Reactive Gas Systems

3.6.1 Leaking Cylinders or Systems

Any leakage from a pressurized cylinder, piping, or other equipment containing toxic or liquefied gas requires immediate action. Leaks of unknown gases or high-hazard gases, or leaks into confined spaces where personnel could be present, require emergency action. In the event of a leak involving an unknown gas or a gas with a health hazard rating of 3 or 4, or in the event of a leak into confined spaces that could be occupied by personnel (regardless of the nature of the cylinder contents), immediately evacuate personnel from the affected area, and dial 911 to notify the Fire Department. Do not attempt to stop the leak yourself.

3.6.2 Emergency Response Responsibilities and Mitigation Options

Gas with a Health Hazard Rating of 2 or Less

Knowledgeable local personnel can attempt to mitigate leaks from cylinders containing gases with a health hazard rating of 2 or less only after notifying their ES&H Team. Mitigation may involve stopping the leak or moving the cylinder to a hood or outside, provided there is no personnel exposure hazard, an explosion, or fire hazard. The ES&H Team representatives will advise on further handling of the cylinder, notification of the Fire Department, and advise about any required incident reporting.

Gas with a Health Hazard Rating of 3 or 4 or an Unknown Gas

In the event of a leak involving gases with a health hazard rating of 3 or 4, or unknown gases, the Fire Department will respond to the 911 call, make an initial assessment of the

situation, and take the necessary action to protect people and contain the hazard. Specifically, the Fire Department will:

- Assume command of the affected area until the leaking cylinder is stabilized or removed.
- Coordinate emergency actions and, if necessary, transport affected persons to the Health Services Department. Individuals in the area may be called upon to help the Fire Department stop a leak and restore normal operations.
- Establish an incident command and evacuate the potentially affected area.

The incident commander (IC) will confer with personnel responsible for the cylinder or gas equipment and the area industrial hygienist, and select a mitigation option (see Table 2) based on the contents of the cylinder, its location, and related hazards.

Once emergency conditions have stabilized, follow the cylinder disposal procedures described in Section 3.2.6.

Table 2. Mitigation options for incidents involving toxic, corrosive, or reactive gases.

For the following conditions	Take the following actions
If removing the cylinder poses a greater hazard to personnel and the environment than simply allowing the cylinder to empty. This could occur in a number of situations such as when 1) the cylinder is completely enclosed in a gas cabinet, 2) there is an explosive hazard or extremely toxic or unknown material, or 3) there is no available method to contain the cylinder.	• Evacuate areas endangered by the leaking gas. • Allow the cylinder to leak until completely empty. • Once the cylinder is completed voided, local personnel may reoccupy the area and replace the empty cylinder if the incident commander has approved reentry after the Hazards Control Department has determined that surface deposits, such as fluorides or arsenic, do not pose a hazard to personnel or has defined appropriate controls. • Contact the area ES&H Team environmental analyst for disposal options. If empty, the cylinder can be handled by local personal.

Adequate PPE, as specified in the HAC is available and personnel have been trained in its use and moving the cylinder will allow normal activities to resume in the area.	• Evacuate areas endangered by the leaking gas. • Remove the cylinder and place in a better-ventilated area (e.g., hood, gas cabinet, or outside). • A cylinder containing a highly toxic or unknown gas shall be removed by Emergency Services and placed in an overpack or LLNL-approved container (if available) for storage prior to emergency treatment. • The incident commander may approve reentry if the Hazards Control Department has determined that surface deposits, such as fluorides or arsenic, do not pose a hazard to personnel or has defined appropriate controls. • Contact the area ES&H Team environmental analyst for disposal options. If empty, the cylinder can be handled by local personnel.

3.7 Transporting Poorly Labeled Cylinders and Cylinders Containing Unknown Gases

Any cylinder whose DOT labels have been damaged or lost or whose contents are unknown shall not be moved or transported. Contact the Fire Department at 911. Contact the ES&H Team for information to implement additional controls that may be needed.

After the analysis is complete, label the cylinder with the correct contents, and handle accordingly.

4.0 Training

Authorizing organizations using toxic, corrosive, or reactive gases shall ensure that operators on every shift are trained to use a self-contained breathing apparatus (SCBA) and other PPE that may be needed to assist the Fire Department during an emergency involving leaking gas. Personnel should also be trained to restore normal operations after an emergency.

Individuals who use toxic, corrosive, or reactive gases shall take the courses listed in Table 3 in accordance with the Document 40.1, "LLNL Training Program Manual," in the *ES&H Manual*. Contact your Hazards Control Department ES&H Team to arrange for the appropriate training. Also see the latest *LLNL Course Catalog*.

Table 3. Training classes for workers who use toxic, corrosive, or reactive gases.

Course #/Title	For those who
EP0006, "Hazardous Waste Generation and Certification"	Generate hazardous or mixed waste or use the toxic, corrosive, or reactive gases covered by this document
HS0032-W, "Facility Safety Plans, Integrated Work Sheets with Safety Plans, and Work Procedures"	Prepare IWSs and SPs.
HS4200, "Hydrofluoric Acid"	Use HF, BF_3, WF_6, or other gases that form HF on contact with water.
HS4240-W, "Chemical Safety"	Use toxic, corrosive, or reactive gases in settings covered by the LLNL HAZCOM Program
HS4246-W, "Laboratory Safety"	Use toxic, corrosive, or reactive gases in settings covered by the LLNL Chemical Hygiene Program
HS4610-CBT[a], "Basic Air Purifying Respirator Training"	May need to use any air purifying respirator.
HS4620-CBT[a], "Basic Air-Supplied Respirator Training"	May need to use any air supplying respirator.
HS4630-S, "SCBA – Interspiro/Spiromatic-Specific"	May need to use a self-contained breathing apparatus.
HS5030-W, "Pressure Safety Orientation"	Handle toxic, corrosive, or reactive gases beyond the limitations specified in Section 3.4, "Reduced Requirements for Brief, Experimental Uses of Toxic, Corrosive, or Reactive Gases."
HS5040-W, "Intermediate Pressure Safety"	Handle toxic, corrosive, or reactive gases beyond the limitations specified in Section 3.4, "Reduced Requirements for Brief, Experimental Uses of Toxic, Corrosive, or Reactive Gases," or if system pressure ranges between 150 and 3000 psig.
HS5060-W, "Pressure Seminar for Engineers"	Design systems and prepare ESNs.
HS5090, "Pressure Installer Course - Certification"	Build or repair toxic gas systems.

[a] This CBT training is provided by Respirator Services just before fit testing is performed.

Using toxic, corrosive, or reactive gases requires specific on-the-job training covering:

- Work procedures and manufacturers' instructions for equipment.
- Relevant SPs or FSPs.
- Relevant material safety data sheets (MSDS).

5.0 Responsibilities

This section describes the responsibilities of personnel who work in areas where exposure to toxic, corrosive, or reactive gases covered is possible. General responsibilities for all workers are described in Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," in the *ES&H Manual*.

The responsibilities of individuals and organizations with regard to the handling of toxic, corrosive, or reactive gases are listed under each title below.

5.1 Workers

- Conduct work in accordance with applicable work plans (e.g., FSPs, SPs, IWSs, HAC forms, and ESNs).
- Be familiar with the hazards of the gases they are using and the controls for those hazards.
- Complete required training.
- Use PPE as required.

5.2 Responsible Individuals

- Complete an IWS and develop safety plans, HACs, and ESNs when required.
- Arrange for the appropriate training specified in Section 4.0.
- Complete a Toxic/Corrosive/Reactive Gases Checklist for each toxic gas purchase request, and ensure that the ES&H industrial hygienist signs the checklist before submitting it to the Industrial Gases Section.
- Following the controls specified in Section 3 of this document. Consultation with the ES&H industrial hygienist early in the planning phase of an experiment will make it easier to meet the administrative control requirements.
- Arrange for proper disposal of used or outdated gas cylinders.
- Initially respond to leaking gas cylinders by evacuating the immediate area and determining the hazard rating of the material involved. Call 911 if the gas has a health or reactivity rating of 3 or 4 or if the incident is serious; call the ES&H Team if the rating is lower.
- Ensure that a ChemTrack bar code is affixed to each cylinder.

- Notify ChemTrack when a cylinder is moved to another location.
- Notify FPOC when purchasing or moving a cylinder to another location.
- Ensure that workers designated to respond to leaking gas incidents requiring SCBA protection take HS4630-S, "SCBA - Interspiro/Spiromatic-Specific."

5.3 Hazards Control Department

5.3.1 ES&H Team

- Assign NFPA/HMIS ratings to gases and gas mixtures.
- Provide guidance to RIs on the content of this document, applicable codes, and dispersion calculations.
- Determine PPE requirements in coordination with gas users.
- Prepare HACs for toxic, corrosive, or reactive gas operations. HACs are mandatory for gases with a hazard rating of 3 or 4.
- Review safety plans and ESNs when necessary.
- Review plans for compliance with NFPA requirements for storage, handling, and use of compressed gases.

5.3.2 Fire Department

The Fire Department responds to incidents involving leaking gas cylinders.

5.3.3 Safety Program Division

The Safety Program Division annually provides the Industrial Gases Section with a list of Industrial Hygienists authorized to sign Toxic/Corrosive/Reactive Gas Checklists.

5.4 Environmental Protection Department

- Provides guidance to RIs on potential hazardous waste, filtration devices, and air-pollution and permitting issues regarding gases.
- Assists RIs with packaging and transporting hazardous waste to RHWM facilities.
- Arranges for the ultimate treatment and disposal of overpacked or patched cylinders.

5.5 Material Distribution Division

5.5.1 Industrial Gases Section

- Ensures cylinders are moved in accordance with the HMPTS.
- Verifies that a cylinder has correct DOT labeling, log the cylinder in ChemTrack, identify the cylinder's contents, place a status tag on the cylinder, and deliver the gas to the designated delivery areas on the same day of arrival (if the gas is a toxic gas) or within one work day of arrival (if the gas is a reactive gas).
- Assists organizations that are planning to move or ship cylinders. The Industrial Gases Section is familiar with DOT shipping regulations, 49 CFR.
- Ensures that ChemTrack bar codes are affixed to each cylinder.

6.0 Work Standards

6.1 Work Smart Standards

29 CFR, Subpart Z, "Toxic and Hazardous Substances," (1910.1000 to 1910.1450 App B), January 1999.

49 CFR, Parts 100-199, "Research and Special Programs Administration, Department of Transportation,"(off-site).

DOE Order 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees," Attachment 2, "Contractor Requirement Document," Sections 1-11, 13-18 (delete item 18.a), 19 (delete item 19.d.3) and 22.

NFPA Standard 13, " Installation of Sprinkler Systems."

NFPA Standard 55, " Compressed and Liquefied Gases in Portable Cylinders."

NFPA Standard 704, "Standard for the Identification of the Fire Hazards of Materials for Emergency Response." Book of SEMI Standards

Standard F4-1990, "Guide for Remotely Actuated Cylinder Valves."

Standard F6-1992, "Guide for Secondary Containment of Hazardous Gas Piping Systems."

Standard F13-1993, "Guide for Gas Source Control Equipment."

Standard F14-1993, "Guide for Gas Source Equipment Enclosures."

Standard S5-1993, "Safety Guidelines for Flow Limiting Devices."

Standard S2-1993, "Safety Guidelines for Semiconductor Manufacturing Equipment."

6.2 Other Required Standards

Book of SEMI Standards

Standard F3-1994, "Guide for Welding Stainless Steel Tubing for Semiconductor Manufacturing Operations."

7.0 Resources for More Information

7.1 Contacts

For more information about the topics described in this document, contact the following:

- ES&H Teams.
- Industrial Gases Section
- Health Services Department.
- Industrial Hygiene, Hazards Control Department.
- Environmental Protection Division.
- Fire Department. For emergencies, dial 911 from within the Laboratory. For non-emergencies, dial (925) 422-5194.
- Shipping Section.
- Alarms Shop.
- C&MS Analytical and Nuclear Chemistry Division.
- Pressure Safety Manager.

7.2 Lessons Learned

Lessons learned applicable to the use of toxic, corrosive, or reactive gases can be found at the following Internet address:

http://www-r.llnl.gov/esh_and_h/lessons/lessons.shtml

7.3 Other Sources

American Society of Heating, Refrigeration, and Air Conditioning Engineers, Chapter 14, *Handbook of Fundamentals*, Atlanta, GA (1993).

National Paint and Coatings Association, *Hazardous Material Identification System Implementation Manual*

Uniform Fire Code, Articles 51, "Semiconductor Fabrication Facilities," and 80, "Hazardous Materials."

Appendix A

Terms and Definitions

Burn box	A device that subjects a gaseous effluent to intense heat created by a flame or heated element. A burn box converts hydrides to oxides (which are usually less toxic than the hydrides), and halocarbons (e.g., Freons and Halons) to hydrogen halides (e.g., hydrogen chloride and hydrogen fluoride). Same as "CDO."
Controlled decomposition/oxidation (CDO) unit	See "Burn box."
Capacity	The internal volume of a cylinder or the volume occupied by the contents of a cylinder before the contents are allowed to expand.
Corrosive	A material which attacks living tissue or common objects. A material is considered to be corrosive if it: 1. Has a pH less than or equal to 2.0 or a pH greater than or equal to 12.5, or if it corrodes steel at a rate greater than 0.25 inches per year or if it burns, irritates, OR 2. Destructively attacks organic tissues, most notably the skin and, if taken internally, the lungs or stomach.
Deflagrate	A violent release of energy where the chemical reaction proceeds at a speed equal to or less than that of sound.
Gas manifold	An apparatus that comprises tubing and associated valves, safety devices, and filters and that is used to deliver gas from a cylinder or source to the tools that use the gas.
Hazardous Materials Information System (HMIS)	A system that uses numbers, letters, and symbols to communicate hazard information. HMIS was developed by the National Paint and Coatings Association, and is based on and similar to the NFPA 704 system. HMIS differs from NFPA 704 by basing the health hazard rating on the potential effects of long-term use of a chemical rather than the effects of a short exposure during fire fighting.

Hazard Assessment and Control Form (HAC)	A document that identifies the hazards and specifies applicable personal protective equipment for a particular operation. The HAC is completed by an ES&H Team industrial hygienist. It can be used to specify controls under specific conditions defined in Section 3.1.1 of this document.
Hazardous waste	Waste that is listed by a regulatory agency or that exhibit a hazardous property.
High-hazard gas	As defined in this document, a gas with an NFPA/HMIS health or reactivity hazard rating of 4.
Hydride	An inorganic compound of hydrogen with another element. Examples include arsine, diborane, silane, and phosphine. Most hydrides are flammable or pyrophoric, and many are highly toxic. (Silane is only moderately toxic.)
Incompatible mixture	A mixture of two or more substances that react together to form heat or produce undesirable reaction products.
NFPA/HMIS fire hazard rating	A rating assigned by the National Fire Protection Association (NFPA) to indicate the flammability hazard of a substance. Ratings range from 0 (nonhazardous) to 4 (extremely hazardous) and can be found in NFPA Standard 704.
NFPA/HMIS health hazard rating	A rating assigned by the NFPA to indicate the health hazard of a substance that fire fighters may encounter. Ratings range from 0 (nonhazardous) to 4 (extremely hazardous) and can be found in NFPA Standard 704. Health hazard ratings assigned by an HMIS may differ because they address the health hazards that users (not fire fighters) may encounter.
NFPA/HMIS reactivity Hazard rating	A rating assigned by the NFPA to indicate the reactivity hazard of a substance that fire fighters may encounter. Ratings range from 0 (nonhazardous) to 4 (extremely hazardous) and can be found in NFPA Standard 704.
NTP	Normal temperature and pressure, which is 760-mm Hg and 25˚C.

Occupational exposure limit (OEL)	The maximum concentration of a substance to which workers can be exposed for a specified time period. Sources of OELs include OSHA statutory regulations and consensus standards developed by various organizations.
Organometallic compound	A compound formed between a metal, carbon, and hydrogen. Examples include methyl arsenic and methyl/ethyl gallium compounds.
Pyrolysis	Decomposition caused by heat.
Pyrophoric gas	A gas that can ignite in air at room temperature even when no flame or other ignition source is present.
Resistant material	A material that will not degrade or fail during anticipated service because of contact with gases or reaction products.
Restrictive Flow Orifice (RFO)	A small round opening of known diameter provided by the vendor of a compressed gas cylinder that limits the maximum attainable flow rate from that cylinder.
Significant quantity	Volume or weight greater than that of one lecture bottle or a cylinder that is approximately 6-in. diameter × 19-in. high.
Toxic, corrosive, or reactive gas	1. A material that can rapidly cause death or serious injury i.e., a material with a reactivity hazard rating of 2 or more, as specified in NFPA Standard 704, a hazardous material information system, or a similar rating scheme that emphasizes long-term exposure hazards, or the equivalent OSHA rating of "toxic" given in 29 CFR 1910.1200, OR 2. A material that has serious long-term toxicity hazards, i.e., a material that warrants a health hazard rating of 3 or 4, as specified in NFPA Standard 704 or a hazardous material information system, or the equivalent OSHA rating of "highly toxic." See also "High-hazard gas."
Toxic gas mixture	A gas mixture whose concentration of a toxic or reactive gas in the cylinder is greater than the applicable OEL for that gas.